

# PATENT SPECIFICATION

(11) 1 285 547

NO DRAWINGS

**1 285 547**

- (21) Application No. 37536/70 (22) Filed 4 Aug. 1970
- (31) Convention Application No. 847 703 (32) Filed 5 Aug. 1969 in
- (33) United States of America (US)
- (45) Complete Specification published 16 Aug. 1972
- (51) International Classification C08B 19/04 25/02 C08K 3/30
- (52) Index at acceptance

C3U 10B 10C 10X 12B1A5 12B1A6B 12B1AX 13 2A1 3C 3D 3E  
 4B2A .4C1 4C2 4C4 4C6 4CX 4M  
 C4X 11  
 D1P A4 B4B C2A12C C2A13B C2A10 C2A4 C2C16 C2C18  
 C2C2 C2C3 C2C5 C2C7 C2C8 C2C9 C2CX



## (54) HAIR SETTING COMPOSITIONS BASED ON CATIONIC HIGH AMYLOSE STARCHES

(71) We, NATIONAL STARCH AND CHEMICAL CORPORATION, a corporation of the State of Delaware, having a place of business at 750 Third Avenue, New York, New York 5 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel hair setting compositions based on high amylose starches containing cationic substituent groups and to a process for setting hair utilizing such 10 compositions.

A hair setting process ordinarily involves the application of an aqueous solution or dispersion of one or more film forming materials to combed hair which has previously 20 been wet or dampened whereupon the thus treated hair is wound on curlers, or the like, and dried. Upon drying, the individual hairs will have a film deposited thereon whose presence will prolong the retentions of curls 25 or other desired configurations in the user's hair. Furthermore, the presence of such films will also impart such desirable properties as body and smoothness.

In order to be effective, the film forming 30 ingredients of a hair setting composition preferably meet a number of requirements. Thus, the films derived from these ingredients should be flexible and yet they should possess strength and elasticity; they should 35 display good adhesion to hair so as to avoid dusting or flaking off with the passage of time or when the hair is subjected to stresses; they should not interfere with the combing and brushing of the hair; they should remain 40 free of tack or gumminess under humid conditions; they should be clear, transparent, and glossy, and maintain their clarity on aging; they should maintain good anti-static properties; and, they should be easily remov-

able by washing with water and either a 45 soap or shampoo.

The present invention provides a hair setting composition comprising an aqueous dispersion containing from 1 to 6%, by weight, of a cationically substituted starch having an amylose content of more than 50% by weight, said cationically substituted starch being selected from primary, secondary, tertiary and quaternary amine derivatives of starch containing from 0.6 to 6%, by weight, of nitrogen; sulfonium derivatives of starch containing from 1.2 to 12%, by weight, of sulfur; and, phosphonium derivatives of starch containing from 1.2 to 12%, by weight of phosphorus.

The invention also provides a hair setting composition comprising an aqueous dispersion containing from 1 to 6%, by weight, of a cationically substituted starch having an amylose content of more than 50% by weight, wherein said cationically substituted starch is also substituted with a non-cationic stabilizing group in a concentration up to a maximum degree of substitution of 0.7, and said cationically substituted starch being selected from primary, secondary, tertiary and quaternary amine derivatives of starch containing from 0.1 to 0.6%, by weight, of nitrogen; sulfonium derivatives of starch containing from 0.2 to 1.2%, by weight, of sulfur; and, phosphonium derivatives of starch containing from 0.2 to 1.2%, by weight, of phosphorus.

The use of certain cationic starches in hair setting compositions has previously been described in U.S. Patent Specification 3,186,911, issued June 1, 1965. However, as set forth in the latter disclosure, it was thought that in order to obtain optimum results, the cationic starches employed in such compositions had to have an amylose content of from 25 to 50%, by weight. Thus, it was considered to be quite critical for the 80 85

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- starch to contain from 50 to 75% by weight of amylopectin in order to be able to provide optimum film forming and adhesive properties.
- 5 In direct contrast to the latter teaching, we have now found that by utilizing cationic starches containing more than 50% by weight, of amylose as the polymeric film forming ingredient it is, in fact, possible to 70
- 10 provide hair setting compositions which are, surprisingly, far superior in their properties to hair setting compositions prepared with starches containing from 25 to 50%, by weight, of amylose. 75
- 15 Thus, as will be shown, hereinbelow, we have found that excellent hair setting compositions can be prepared with cationic starches which do not contain a high proportion of amylopectin. 80
- 20 Moreover, it has been found, unexpectedly, that in addition to serving as hair setting compositions, the novel compositions of this invention may also be utilized as a creme rinse which is applied after the user's hair has been washed. In this function, the compositions of this invention serve as a means of effectively balancing or neutralizing the inherent negative charge of the hair, thereby imparting a smoothness and lubricity to wet 85
- 25 hair which permits it to be combed without snarling or tangling. When the treated hair has been dried, the film which has been deposited serves to maintain an electrically neutral balance and provides it with a desirable silky resiliency. 90
- 30 The starch bases which may be used to prepare the cationic derivatives useful in the hair setting compositions of this invention may be derived from any of the usual sources, including corn, wheat, potato, tapioca, sago and rice. It is only necessary, however, that the selected starch base contain more than 50%, by weight, of amylose. Pure amylose resulting from the fractionation of starch into its amylose and amylopectin components may also be utilized although economic considerations generally preclude its use on a commercial basis. Mixtures of such starch bases may also be 95
- 35 utilized. These starch bases may be used in their original raw form or even subsequent to their being treated as, for example, by being dextrinized, hydrolyzed, inhibited, esterified or etherified provided that they are still capable of further derivatization into cationic derivatives of the type described below. 100
- 40 The present invention comprises the use, as the film forming ingredient of novel hair setting compositions, of high amylose starch derivatives containing cationic substituent groups, that is chemical groups which serve to introduce a positive electrical charge into the starch molecule. Optionally, such 105
- 45 starch derivatives may be used in their original raw form or even subsequent to their being treated as, for example, by being dextrinized, hydrolyzed, inhibited, esterified or etherified provided that they are still capable of further derivatization into cationic derivatives of the type described below. 110
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- 65 starch derivatives may be used in their original raw form or even subsequent to their being treated as, for example, by being dextrinized, hydrolyzed, inhibited, esterified or etherified provided that they are still capable of further derivatization into cationic derivatives of the type described below.
- The cationic starch derivatives may be prepared, for example, by reacting starch, ordinarily through an etherification or esterification reaction, with any reagent which will introduce into the starch a primary, secondary, tertiary, or quaternary amine group, or a sulfonium or phosphonium group. A preferred class of cationic starch derivatives are the tertiary amino alkyl ethers resulting from the reaction of starch, under alkaline conditions, with a dialkyl amino alkyl epoxide or dialkyl amino alkyl halide; or the corresponding compounds containing aryl groups in addition to the alkyl groups. The latter derivatives correspond to the formula
- $X - O - R - N R_1 R_2$
- wherein X is starch, R is an alkylene or hydroxyalkylene radical, and each of R<sub>1</sub> and R<sub>2</sub> is an alkyl, aryl or aralkyl radical. The latter derivatives and their preparation are described in U.S. Patent 2,813,093, issued November 12, 1957.
- Although these tertiary amino alkyl ethers for starch are preferred for use in our hair setting compositions, primary and secondary amine derivatives as well as cationic starch esters may also be used.
- Thus, besides the reagents already named one may react starch with amino alkyl anhydrides, alkyl imines, amino alkyl epoxides, amino alkyl halides, alkyl amino alkyl epoxides (or halides), amino alkyl sulfates, and the corresponding compounds containing aryl in addition to alkyl groups. As previously pointed out the sulphonium and phosphonium derivatives of starch are also cationic and therefore suitable for the purposes of this invention. The preparation of sulphonium derivatives of starch is described in U.S. Patent 2,989,520, issued June 20, 1961 and involves, essentially, the reaction of starch, in an aqueous alkaline medium, with a beta-halogeno alkyl sulfonium salt, vinyl sulfonium salt or epoxy alkyl sulfonium salt.
- The preparation of phosphonium derivatives of starch is described in U.S. Patent 3,077,469, issued February 12, 1963, and essentially involves the reaction of starch, in an aqueous alkaline medium, with specified phosphorus containing reagents.
- Other suitable starch derivatives will be apparent to the practitioner, since any starch derivative which has been rendered cationic by the introduction of a positive, electrically charged moiety into the starch molecule may be utilized in the present compositions.
- Returning now to the class of cationic starch derivatives containing amine groups,

- the following are some representative reagents which may be reacted with starch to result in such derivatives: ethylene imine; propylene imine; isatoic anhydride; quinolinic anhydride; beta diethyl amino ethyl chloride; beta dimethyl amino isopropyl chloride; beta dimethyl amino ethyl chloride; 3-diethyl amino 1,2-epoxypropane; 3-dibutyl amino 1,2-epoxypropane; 2-bromo-5-diethyl amino pentane hydrobromide; N-(2,3-epoxypropyl)piperidine; N,N-(2,3-epoxypropyl)methyl aniline. The various halides (e.g. chloro-, bromo-, etc.) can be used interchangeably. In the above reagents, where the free amines have been indicated (e.g., beta diethyl amino ethyl chloride), one can also use the hydrochloride or other salts of these reagents (e.g., beta diethyl amino ethyl chloride hydrochloride). In fact, it is ordinarily preferred to use the salts since these tend to be less toxic and more easily handled. The hydrochloride moiety takes no part in the reaction with the starch. It will be seen that beside the alkyl, aryl and aralkyl types, the reagents may also include those containing cyclic groups. Therefore, when reference is made herein to the alkyl, aryl or aralkyl groups, it will be understood that these cyclic reagents are equivalents of those types.
- It should also be mentioned that the starch-amine products may be subsequently treated by known methods, as by the use of an alkyl halide, so as to result in producing the quaternary ammonium salt; or, such a quaternary ammonium salt may be made directly from raw starch by treating it with the reaction product of an epichlorohydrin and a tertiary amine or tertiary amine salt. In either case the resulting starch derivative is, of course, cationic.
- To be suitable for use in our novel hair setting compositions, the high amylose starches may be substituted with cationic groups to the extent that the starches contain from 0.6 to 6%, by weight, of nitrogen; from 1.2 to 12%, by weight, of sulfur; or, from 1.2 to 12%, by weight, of phosphorus; depending, of course, as to whether the elected cationic substituent group contains nitrogen, sulfur, or phosphorus.
- The hair setting compositions of this invention are prepared by dispersing the selected high amylose cationic starch derivative in cold water and then heating the resulting dispersion to a temperature of 90 to 100°C. for a period of from 20 to 30 minutes. No pressure cooking or high temperature cooking is ordinarily required. These dispersions will usually contain 1 part of starch to 20 to 30 parts of water on a weight basis. After cooling to room temperature and diluting with additional water, if necessary, the resulting starch dispersion is ready for use unless the addition of optional ingredients, as described hereinbelow, is desired. Useful concentrations of starch in the final hair setting composition may vary from 1 to 6%, by weight, with 1.5 to 4%, by weight, being preferred.
- It is to be noted that the high amylose starches which have been derivatized to contain cationic substituents may be gelatinized prior to their being utilized in the present hair setting compositions. The gelatinization may be effected, for example, by passing an aqueous slurry of the starch over heated rollers which raise the temperature of the slurry above the gelatinization point of the starch present therein while also evaporating the water therefrom so as to ultimately yield dry, solid particles of pregelatinized starch. Such gelatinized starches are commonly preferred to as cold water swelling or pre-gelatinized starches.
- The procedure for preparing the hair setting compositions of this invention with such pregelatinized high amylose cationic starches involves the admixture and dispersion of the pregelatinized starch in cold water, diluting the resulting dispersion to the proper concentration and the addition, if desired, of any optional ingredients.
- We have found that in addition to the above described cationic starches, we can also utilize those high amylose starches which have been cationically substituted to a lesser extent than specified hereinabove. Thus, we can utilize cationic starches having a nitrogen content of 0.1 to 0.6%, by weight, or a sulfur content of 0.2 to 1.2%, by weight, or a phosphorus content of 0.2 to 1.2%, by weight, provided, however, that the latter low substituted cationic derivatives have been subjected to an additional step which introduces non-cationic substituent groups, such as ester or ether groups, or any other non-cationic substituent group to the starch molecule which will serve to stabilize the low substituted cationic starch derivative. Among the applicable starch ester stabilizing groups are included acetate, propionate, butyrate, laurate, stearate, and oleate groups. Among the applicable starch ether stabilizing groups are included methyl, ethyl, propyl, hydroxyethyl, carboxymethyl and hydroxypropyl groups. The "stabilizing" effect here being referred to is the property which enables compositions containing such starches to maintain their viscosity without any significant gelling over prolonged periods of time.
- The cationic starches used in or compositions may contain the stabilizing substituent group in a concentration ranging up to a maximum degree of substitution of 0.7.
- In order to prepare such a disubstituted starch, i.e. stabilized, cationic starch, such, for example, as a hydroxyalkyl substituted cationic starch, a low substituted tertiary amino alkyl ether cationic starch may be reacted with an alkylene oxide, such as

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ethylene or propylene oxide, in an aqueous alkaline media. The detailed procedures which may be used in preparing such hydroxyalkyl starch derivatives are described in U.S. Patents 2,516,632; 2,516,633; and 2,516,634. On completion of the hydroxyalkylation procedure, the resulting derivative, which now contains hydroxyalkyl as well as tertiary amino alkyl ether substituent groups, is subsequently cooked in the usual manner, as described hereinabove, and yields compositions which are comparable in their film forming properties to compositions prepared using the more highly substituted cationic starches which do not require stabilization in this manner.

The sequence in which the reactions utilized to produce the stabilized cationic derivatives of these high amylose starches is carried out may be critical in some instances. As those skilled in the art will recognize, reactions in alkaline media carried out on esterified starches will often lead to loss of the ester group. Thus, for example, a starch which contains cationic ester groups cannot subsequently be reacted with an alkylene oxide under the required alkaline conditions.

The hair setting compositions of this invention may, if desired, contain a number of optional ingredients in order to modify certain of their properties. Thus, they may contain hair conditioning agents such as alkoxyLATED lanolin and stearyl dimethyl benzyl ammonium chloride; plasticizers such as urea and polyoxyethylene glycol stearate; preservatives such as methyl and propyl hydroxybenzoates; dyes; lower aliphatic alcohols; and perfumes.

With regard to the actual use of the hair setting composition of this invention, ordinarily a portion of 10 to 40 milliliters of the final composition is applied directly to the user's wet hair and is worked through by massaging with the fingers. The hair is then combed, set with curlers or by other means into a desired configuration and dried in any conventional manner such, for example, as with the use of a hair dryer. When the hair is dry it may then be combed or brushed.

The precise details of the above-described procedure are not particularly critical, it merely being necessary that our novel hair setting composition is applied to the moistened hair whereupon the thus treated hair is subsequently set into any desired configuration and then dried so as to ultimately result in the deposition of a film upon the individual hairs of the user; the resulting film serving to retain the user's hair in the desired configuration. It can be appreciated that any means which accomplish the essential features of this procedure will be effective.

It is to be noted that the above described high amylose cationic starch derivatives are likewise capable of being admixed with aerosol propellants so as to produce aerosol hair spray compositions which may be conveniently applied from a suitable aerosol dispenser and thereby provide a means for the maintenance of the hair configuration. In order to utilize these cationic starches in aerosol formulations, a cooked dispersion of the starch, containing 1 part of starch to 10 to 30 parts of water is prepared, as described hereinabove, and is then cooled to room temperature and diluted with about an equal volume of isopropyl or, more preferably, ethyl alcohol. The resultant alcoholic dispersion is then charged into a suitable aerosol-type container together with an aerosol propellant such, for example, as a low boiling hydrocarbon or a halogenated hydrocarbon or any desired mixture thereof. Examples of such low boiling hydrocarbons include propane, butane and isobutane while typical halogenated hydrocarbons include trichloromonofluoromethane and dichlorotetrafluoroethane. The concentration of starch in these aerosol formulations is from 1 to 4% of their total weight. Needless to say, the aerosol formulations may also contain any desired optional ingredients as described hereinabove.

The embodiment of this invention is illustrated in more detail by the following examples wherein all parts given are by weight unless otherwise noted. All of the high amylose starches used in these examples were cationically substituted so as to contain either nitrogen or sulfur within the limits for these respective elements as specified hereinabove.

#### EXAMPLE I

This example illustrates the preparation of a hair setting composition typical of this invention which was based upon a tertiary amino alkyl ether of a high amylose corn starch.

Three parts of corn starch containing 70%, by weight, of amylose, which had been etherified so as to introduce diethyl amino ethyl substituent groups by means of the procedure described in Example I of U.S. Patent No. 2,813,093, was dispersed in 6 parts of cold water. An additional 91 parts of water was then added and the mixture was dispersed by heating at 95 to 100°C. for a period of about 25 minutes. At the end of this period, the mixture was cooled and diluted with an additional 50 parts of water so as to contain about 2 parts of dry starch per 100 parts of water. The resulting dispersion displayed excellent stability with no tendency to gel and was used as a hair setting composition.

In order to determine the effectiveness of this product as a creme rinse and hair

setting composition, the following test was carried out.

*Creme Rinse and Curl Retention Test:*

5      Swatches of European human hair each weighing 2 grams were firmly bound at the root end, suspended from a horizontal bar, wet with distilled water, combed, and cut to so as to measure 10 inches in length. Each swatch was then washed  
 10     with a shampoo and thoroughly rinsed with water. The particular hair setting composition being evaluated was then applied by pouring a small amount directly onto the swatch and massaging the hair  
 15     with the fingers so as to effect its even distribution. The wet swatches were then combed and observations on the tendency to tangle or snarl were recorded. Snarled hair could not, of course, be easily combed. Each composition which was tested was rated as either poor, fair, good, or excellent with respect to its wet combing properties. The combed, wet swatch  
 20     was next wound on a polytetrafluoroethylene mandrel having a one-half inch diameter, after which the mandrel was removed while the curl was secured with a clip. The thus treated curl was dried at 140°F. for a period of 30 minutes and then conditioned for 16 hours at 72°F.  
 25     and a relative humidity of 50%. After the conditioning period was completed, the clip was removed and the curl was unwound thus forming a loose spiral. The curl was measured for initial length ( $L_0$ ) and then placed in a cabinet wherein the temperature was maintained at 72°F. and the relative humidity at 90%. The length of the curl was recorded at thirty  
 30     minute intervals over a period of 180 minutes. To calculate the percent curl retention, the following formula was used:

$$\text{Percent Curl Retention} = \frac{(L - L_0) / 100}{(L - L_0)}$$

45     where

$L$  = length of hair fully extended,  
 $L_0$  = length of hair before exposure of 90% relative humidity,  
 50      $L_t$  = length of hair after exposure to 90% relative humidity.

When the above-described cationic high amylose starch based hair setting composition was evaluated by means of this creme rinse and curl retention test, the mean curl retention of 8 replicates at 30 minutes was found to be 80.2% while at 180 minutes it was found to be 62.4%. Its wet combing properties were rated as good. For comparison purposes, a comparable hair setting composition was prepared which, in this

instance, utilized ordinary corn starch containing only 25%, by weight, of amylose and which had been etherified so as to introduce diethyl amino ethyl substituent groups by means of the procedure described in Example I of U.S. Patent No. 2,813,093. When the latter composition was evaluated by means of the creme rinse and curl retention test described hereinabove, the mean curl retention of 8 replicates at 30 minutes was found to be only 35.1% while at 180 minutes it was found to be only 29.0%. Moreover, its wet combing properties were rated as poor.

The results of the above-described evaluation demonstrate the significantly improved curl retention and wet combing properties that are achieved using compositions prepared with cationic high amylose starches as compared to compositions prepared with conventional, low amylose starches which had been substituted to contain the identical cationic substituent groups.

**EXAMPLE II**

This example illustrates additional compositions, representative of this invention, which were prepared using a variety of high amylose starches which had been substituted with various cationic substituent groups.

The procedure set forth in Example I, hereinabove, was utilized in preparing each of the below described compositions. Various optional ingredients were blended into the diluted dispersions in order to produce the final composition. The percent curl retention values are provided in order to characterize each of the thus prepared compositions.

*Composition A:*

	<i>Parts</i>
Corn starch containing 56.5%, by weight, of amylose, which had been etherified so as to introduce diethyl amino ethyl substituent groups by means of the procedure described in U.S. Patent No. 2,813,093 ...	100
Ethoxylated lanolin ... ... ...	105
Perfume ... ... ... ...	4
Water ... ... ... ...	1
	1
	194

*Composition B:*

	<i>Parts</i>
Corn starch containing 80%, by weight, of amylose; which had been etherified so as to introduce diethyl amino ethyl substituent groups by means of the procedure described in U.S. Patent No. 2,813,093 ...	115
Stearyl dimethyl benzyl ammonium chloride ... ... ...	3
Anhydrous ethanol ... ... ...	10
Perfume ... ... ... ...	120
Water ... ... ... ...	1
	183

Composition C:		Parts	Composition D: (Contd.)		Parts
5	Corn starch containing 70%, by weight, of amylose, which had been etherified so as to introduce quaternary ammonium salt substituent groups by means of the procedure described in Example VI of U.S. Patent No. 2,813,093	3	No. 2,989,520	...	3
10	Polyoxyethylene glycol stearate	1	Staryl dimethyl benzyl ammonium chloride	...	3
	Perfume	1	Perfume	...	1
	Water	195	Water	...	193
Composition D:		Parts	Composition E:		Parts
15	Corn starch containing 70%, by weight, of amylose, which had been etherified so as to introduce sulfonium substituent groups by means of the procedure described in U.S. Patent No. 2,813,093	2	Amylose fraction of corn starch which had etherified so as to introduce diethyl amino ethyl substituent groups by means of the procedure described in U.S. Patent No. 2,813,093	...	1
	Ethoxylated lanolin	1	Ethoxylated lanolin	...	97
	Water	195	Water	...	30
The resulting compositions displayed the following values when they were evaluated in the curl retention test described in Example I, hereinabove.					
TABLE I					
40	Composition	Percent Curl Retention (at 90% Rel.Hum.)			
		After 30 minutes		After 180 minutes	
45	A	64.0		49.0	
	B	61.4		47.0	
	C	58.1		42.7	
	D	68.2		48.3	
	E	66.0		47.0	
	Control*	35.1		29.0	

Thus, the data summarized hereinabove clearly point out that the compositions of the present invention all displayed superior curl retention properties when compared with the comparable compositions based on a conventional, low amylose starch.

### EXAMPLE III

This example illustrates the preparation of hair setting compositions based upon starches which were substituted so as to contain both cationic and hydroxyalkyl substituent groups.

Six parts of corn starch containing 58%, by weight, of amylose, which had been etherified by means of the procedure described in Example I of U.S. Patent No. 2,813,093 so as to introduce diethyl amino ethyl substituent groups to the extent that its Kjeldahl nitrogen content was 0.17%, by weight, and which had been further derivatized with 9%, by weight, of propylene oxide so as to provide the resulting reaction product with hydroxypropyl groups in a D.S. of 0.2, was dispersed in 8 parts of

cold water. An additional 92 parts of water was then added and the mixture was dispersed by heating at about 95 to 100°C. for a period of 25 minutes. At the end of this period, the mixture was cooled and diluted with an additional 10 parts of water so as to contain about 5.5 parts of dry starch per 100 parts of water.

In a variation of the above procedure, 4 parts of corn starch containing 70%, by weight, of amylose, which had been derivatized with propylene oxide so as to provide the resulting reaction product with hydroxy-propyl groups in a D.S. of 0.7 and was further etherified by means of the procedure described in U.S. Patent No. 2,813,093, so as to introduce diethyl amino ethyl substituent groups to the extent that its Kjeldahl nitrogen content was 0.15%, by weight, was dispersed in 8 parts of cold water. An additional 88 parts of water was then added thereto and this mixture was dispersed by heating it at about 95 to 100°C. for a period of 25 minutes. At the end of this period, the mixture was cooled and diluted with an addi-

TABLE I

**40**      Composition      Percent Curl Retention (at 90% Rel.Hum.)  
                                   After 30 minutes      After 180 minutes

	A	64.0	49.0
	B	61.4	47.0
	C	58.1	42.7
	D	68.2	48.3
	E	66.0	47.0
45	Control*	35.1	29.0

\*The control composition utilized ordinary corn starch containing 25%, by weight, of amylose which had been etherified to introduce diethyl amino ethyl substituent groups.

### EXAMPLE III

This example illustrates the preparation of hair setting compositions based upon starches which were substituted so as to contain both cationic and hydroxyalkyl substituent groups.

Six parts of corn starch containing 58%, by weight, of amylose, which had been etherified by means of the procedure described in Example I of U.S. Patent No. 2,813,093 so as to introduce diethyl amino ethyl substituent groups to the extent that its Kjeldahl nitrogen content was 0.17%, by weight, and which had been further derivatized with 9%, by weight, of propylene oxide so as to provide the resulting reaction product with hydroxypropyl groups in a D.S. of 0.2, was dispersed in 8 parts of

In a variation of the above procedure, 4 parts of corn starch containing 70%, by weight, of amylose, which had been derivatized with propylene oxide so as to provide the resulting reaction product with hydroxy-propyl groups in a D.S. of 0.7 and was further etherified by means of the procedure described in U.S. Patent No. 2,813,093, so as to introduce diethyl amino ethyl substituent groups to the extent that its Kjeldahl nitrogen content was 0.15%, by weight, was dispersed in 8 parts of cold water. An additional 88 parts of water was then added thereto and this mixture was dispersed by heating it at about 95 to 100°C. for a period of 25 minutes. At the end of this period, the mixture was cooled and diluted with an addi-

tional 60 parts of water so as to contain about 2.5 parts of dry starch per 100 parts of water.

Both of the resulting dispersions displayed excellent stability and were ready for use as hair setting compositions.

When evaluated in the previously described creme rinse and curl retention test, each of these compositions was found to exhibit wet combing and curl retention properties comparable to those of the compositions of Example II, hereinabove.

#### EXAMPLE IV

This example illustrates the preparation of a hair setting composition based upon a cationic high amylose starch which, in this case, was in the form of an aerosol formulation. A total of 1.4 parts of corn starch containing 56.5%, by weight, of amylose which had been etherified so as to introduce diethyl amino ethyl substituent groups was dispersed in 35 parts of cold water and heated to about 95°C. for a period of 30 minutes. At the end of this period the mixture was cooled and 33.46 parts of ethanol and 0.14 parts of polyoxyethylene glycol stearate were admixed. The resultant homogeneous mixture was placed in an aerosol container which was then charged with a propellant mixture comprising 27 parts of isobutane and 3 parts of propane whereupon the container was sealed. The resulting aerosol formulation provided excellent results as a hair setting composition.

Summarizing, it is seen that this invention based on high amylose starches which have provides novel hair setting compositions been chemically substituted so as to contain cationic substituents.

#### WHAT WE CLAIM IS:—

1. A hair setting composition comprising an aqueous dispersion containing from 1 to 6%, by weight, of a cationically substituted starch having an amylose content of more than 50%, by weight, said cationically substituted starch being selected from primary, secondary, tertiary and quaternary amine derivatives of starch containing from 0.6 to 6%, by weight, of nitrogen; sulfonium de-

rivatives of starch containing from 1.2 to 12%, by weight, of sulfur, and, phosphonium derivatives of starch containing from 1.2 to 12%, by weight, of phosphorus.

2. A hair setting composition comprising an aqueous dispersion containing from 1 to 6% by weight, of a cationically substituted starch having an amylose content of more than 50% by weight, wherein said cationically substituted starch is also substituted with a non-cationic stabilizing group in a concentration up to a maximum degree of substitution of 0.7 and said cationically substituted starch being selected from primary, secondary, tertiary, and quaternary amine derivatives of starch containing from 0.1 to 0.6%, by weight, of nitrogen; sulfonium derivatives of starch containing from 0.2 to 1.2%, by weight, of sulfur; and, phosphonium derivatives of starch containing from 0.2 to 1.2%, by weight, of phosphorus.

3. The hair setting composition of claim 1 or 2, wherein said aqueous dispersion contains from 1 to 4%, by weight, of said cationically substituted starch and also contains ethyl alcohol or isopropyl alcohol as well as an aerosol propellant.

4. The hair setting composition of any preceding claim wherein said cationically substituted starch corresponds to the formula



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wherein X is starch, R is an alkylene or hydroxyalkylene radical, and each of R<sub>1</sub> and R<sub>2</sub> is an alkyl, aryl or aralkyl radical.

5. A method for setting hair which comprises applying to the hair the hair setting composition of any preceding claim, setting the hair to the desired configuration and drying the thus treated hair.

6. The hair setting composition of claim 1 or claim 2 substantially as described in any of Examples I to IV.

For the Applicants:—  
 A. POOLE & CO.,  
 Chartered Patent Agents,  
 19 Devonshire Street,  
 London, W.1.

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 Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY  
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